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- (71) Applicant (for all designated States except US): ORB-SEAL LLC [US/US]; 210 E. HWY 10, Richmond, MO 64085 (US).
- (71) Applicants and  
(72) Inventors: DUFFIN, Gary, Raymond [US/US]; 1933 Marvel Lane, Liberty, MO 64068 (US). LUPINI, Michael, Allen [US/US]; 140 Marlene Street, Milford, MI 48386 (US). TAYLOR, Donald, W. [US/US]; 1129 Camelot Hills, Liberty, MO 64068 (US). TKACZ, Peter [AU/GB]; 296 Bilton Road, Rudgy, Warwickshire, CV22 7EJ (GB).
- (74) Agent: BOYER, Michael, Kevin: Chief Patent Counsel, Orscheln Management Co. 2000 U.S. Highway 63 South, Moberly, MO 65270 (US).
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**WO 01/30906 A1**

(54) Title: EXPANDABLE COMPOSITIONS AND METHODS OF MAKING AND USING THE COMPOSITIONS

(57) Abstract: A novel expandable composition and method for using the same are disclosed. The disclosed method relates to using the composition, for example, as an automotive cavity sealant. The inventive composition normally is a combination of at least one base polymer, at least one expansion or blowing agents, at least one hydrocarbon resin, at least one curing agent or catalyst and optionally at least one additive such as a supplemental polymer, colorant, tackifier, processing oil, among others.

TITLEEXPANDABLE COMPOSITIONS AND METHODS OF  
5 MAKING AND USING THE COMPOSITIONS

The subject matter herein claims benefit of prior filed U.S. Patent  
Application Serial Nos. 60/161,528, filed on October 26, 1999 and 60/219,095,  
filed on July 18, 2000; the disclosure of which is hereby incorporated by reference.

FIELD OF THE INVENTION

The instant invention relates to a novel expandable composition. The  
instant invention also relates to a method of using the composition, for example, as  
an automotive cavity sealant.

BACKGROUND OF THE INVENTION

Expandable sealants are known in this art such as described in U.S. Patent  
Nos. 4,427,481; 4,874,650; 5,266,133; 5,373,027; 5,506,025; 5,266,133;  
5,373,027; and 5,678,826; and European Patent No. EP 0 730 998B1; the  
20 disclosure of each of which is hereby incorporated by reference. One conventional  
cavity sealing arrangement and method is described in U.S. Patent No. 5,040,803;  
the disclosure of which is also hereby incorporated by reference. Other convention  
cavity sealants comprise polyvinyl chloride (PVC) based materials that are pumped  
into location and, in some cases, expand after being exposed to a sufficient amount  
25 of heat. Conventional sealants also include polyurethane based or containing  
foams. Typically, these sealants are employed in automotive applications for filling  
cavities, stiffening adjacent components and dampening sound/vibrations.

Conventional sealant compositions may be limited in their application due to the temperature and time required to cause the sealant to expand. Certain conventional compositions also require the addition of heat to produce the expandable composition as well as to cause the composition to expand. There is a  
5 need in this art for an expandable composition that: 1) is activated at a relatively low temperature, 2) adheres to a metal substrate, 3) is easily installed and remains in a predetermined location and 4) for some applications is resistant to fuel, e.g., diesel and gasoline.

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### SUMMARY OF THE INVENTION

The instant invention solves problems associated with conventional sealants and methods by providing a novel composition that can be molded into a predetermined shape and expanded by being exposed to a sufficient amount of heat, e.g., an external source of heat. In contrast to conventional sealants, the  
15 inventive composition can: 1) have a predetermined shape, e.g., by injection molding, 2) located, e.g., within a cavity, or around or upon a member to be sealed, prior to/post assembly while remaining in a predetermined location, 3) employed in a wide range of applications, 4) produced at relatively low temperatures; 5) expanded at relatively low temperatures, e.g., after being installed within a cavity;  
20 and 6) recycled as scrap material post cure.

The inventive composition may be employed in automotive applications, e.g., the composition may be used in accordance with the guidelines set forth in Ford Specification No. ESB-M 18P11 A, WSB-M 18P11A2, General Motors Specification No. 9984188 C/D/G and DaimlerChrysler Specification No. MS-CD  
25 627 B/E, 644, and 466; the disclosure of these Specifications is hereby incorporated by reference.

By tailoring the inventive composition, the expansion initiation temperature of the composition, degree of expansion, time until fully expanded, among other

processing characteristics, can be predetermined to satisfy a wide range of end-uses. The inventive composition can expand about 450 to about 800 volume % at temperatures of about 250 to about 375 F (adjacent metal temperature), depending upon the characteristics of the composition. When the heat of expansion is  
5 provided from a powder coat system, the temperature can be 385F to about 400F. For example, the inventive composition can expand at least about 500% at a temperature of about 300 F. Depending upon the desired expansion rate and expansion initiation temperature, the inventive composition can be tailored to expand 800 to 1,000% and have expansion initiation temperatures from about 120  
10 to 170C (adjacent metal temperature).

### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is an end-view of a cross-section of one aspect of the instant invention.

15 Figure 1B is a side-view of the product illustrated in Figure 1A.

Figure 2A is an end-view of a cross-section of another aspect of the instant invention.

Figure 2B is a side-view of the product illustrated in Figure 2A.

Figure 3A is a first side-view of a further aspect of the instant invention  
20 that includes a fastener for use in sealing an automotive A-pillar.

Figure 3B is a second side-view of the product illustrated in Figure 3A.

Figure 3C is an end-view of the product illustrated in Figure 3A.

Figure 4A is a first side-view of a further aspect of the instant invention that includes a fastener for use in sealing an automotive front B-pillar.

25 Figure 4B is a second side-view of the product illustrated in Figure 4A.

Figure 4C is an end-view of the product illustrated in Figure 4A.

Figure 5A is a first side-view of a further aspect of the instant invention that includes a fastener for use in sealing an automotive C-pillar.

Figure 5B is a second side-view of the product illustrated in Figure 5A.

Figure 5C is an end-view of the product illustrated in Figure 5A.

Figure 6 is an overhead view of a further aspect of the instant invention that can be compression fit within a cavity.

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### DETAILED DESCRIPTION

The inventive composition broadly comprises a combination of at least one base polymer, at least one expansion or blowing agents, at least one hydrocarbon resin, at least one curing agent or catalyst and optionally at least one additives such as a supplemental polymer, colorant, tackifier, processing oil, among others.

While any suitable base polymer or mixtures thereof can be employed, an examples of suitable polymers comprise at least one member from the group of styrene butadiene rubber, a modified ethylene copolymer blend such as maleic anhydride modified copolymer of ethylene and vinyl acetate, among others. Such polymers are available commercially as Bynel™ CXA 3860 (supplied by The DuPont Company, Wilmington, Delaware). Normally, the base polymer corresponds to about 55 to about 84 wt.% of the composition prior to expansion. When a fuel resistant composition is desired, a base polymer can comprise at least one member selected from the group consisting of epoxies, epoxy functional compounds, modified polyethylene blends, mixtures thereof, among others.

Any suitable expansion or blowing agent can be employed that becomes or generates a gaseous or vapor phase (e.g., nitrogen, carbon dioxide, etc.), when exposed to a sufficient amount of heat. Examples of such expansion agents comprise at least one of azodicarbonamides and p,p'-oxybis(benzene-sulfonyl hydrazide) or diphenylozide-4, 4'-disulphohydrazides supplied, respectively, by Uniroyal as Celogen™ 765 and Celogen™ OT. Typically, the expansion agent comprises about 1 to about 15 wt.% of the composition prior to expansion. The amount of expansion agent can be tailored depending upon the temperature/time,

desired degree of expansion, time permitted for expansion, among other parameters. Generally, higher concentrations of Celogen™ OT are employed in conjunction with urea (e.g., BIK OT supplied by Uniroyal Chemical Company) for relatively low temperature expansion whereas Celogen™ 765 accommodates  
5 higher temperature expansion.

In some cases, the expansion or blowing agent has been treated. By treated it is meant that the expansion or blowing agent has been contacted or admixed with a suitable binder, e.g, binder comprising at least one of naphthenic, glycerins, polyols, ethylene propylene monomer, paraffinic, among others. For example, an  
10 expansion agent comprising Celogen™ OT has been admixed with a naphthenic binder for safety and dispersion. Examples of suitable binders comprise those commercially supplied by Polychem, PPD celot 90, ElastoChem, OT-72 AkroChem, and mixtures thereof. The ratio of expansion agent to binder normally ranges from about 5 to about 30%. Notwithstanding the binder the expansion  
15 agent is typically at least about 90% active.

Moreover, the expansion or blowing agent can be encapsulated within a shell. That is, a liquid or gaseous blowing agent is combined with or encapsulated within a thermoplastic particle or powder, e.g., a hydrocarbon encapsulated within an acrylonitrile shell as in Expancel® that is supplied by Expancel Inc., a division of Akzo  
20 Nobel Industries. For example, the shells can be fabricated from polyolefins such as polyethylene and polypropylene; vinyls, EVA, nylon, acrylics, among other materials. The shells are selected to melt, soften, expand, rupture or retain their physical configuration depending upon whether or not an open or a closed cell expanded material is desired. The shells can also comprise a distribution of differing particle sizes,  
25 composition and activation temperatures, e.g., a foam precursor comprising at least two different particle sizes and activation temperatures. Specific examples of suitable encapsulated blowing agents comprise at least one member selected from the group of hydrocarbons such as isobutane and isopentane; fluorocarbons such as 1,1-dichloroethene, HFC-134a, HFC-152a; and nitrogen releasing chemical blowing agents such as those

supplied as Celogen® by UniRoyal that are encapsulated within any suitable thermoplastic, e.g., 2-methyl 2-propenoioc acid methyl ester polymer with 2-propenenitrile and vinylidene chloride polymer and polyvinylidene fluoride. These materials are supplied commercially by Expancel, Inc., a division of Akzo Nobel as Expancels®

5 051WU, 051DU, 091DU80, 820WU, 820DU, 642WU, 551WU, 551WU80, 461DU or Micropearl® F30D supplied by Pierce and Stevens. These materials can be supplied in either dry or wet form. These materials can also be coated with any suitable material for controlling the activation temperature of the encapsulated blowing agents. An example of a coating comprises an acrylated materials, waxes, among other materials. Depending

10 upon the physical characteristics desired in the foam, the shells can be used to obtain open or closed cells.

The inventive composition can comprise any suitable hydrocarbon resin or mixtures thereof that accommodates the expansion temperature, e.g, at least about 300 F. Examples of suitable resins are rosin esters, polyterpenes, an aliphatic or

15 aromatic hydrocarbon resins, e.g, C5 to C9 hydrocarbon and aromatically modified hydrocarbon resins, mixtures thereof, among others. Suitable resins are available commercially as Piccotac® supplied by Hercules Incorporated, Wilmington, Delaware or Escorez® supplied by Exxon Chemical Co., Houston, TX, Zonester® by Arizona Chemicals, and Wingtac® by Goodyear. Normally, for best results, the

20 hydrocarbon resin can be crushed or ground to form a particulate material, e.g., the particle size normally pass through 80% at 40 mesh and 100% at 30 mesh. The hydrocarbon resin can comprise or consist essentially of about 1 to about 15 wt.% of the inventive composition prior to expansion.

The inventive composition normally comprises at least one curing agent or

25 catalyst such as tetramethylthiuram disulfide, e.g., TMTD applied by Akrochem Corporation, Akron, Ohio, organic peroxide by AkroChem, and urea or urea modified materials (e.g., surface treated), e.g., BIK-OT by Uniroyal Chemical Company. Without wishing to be bound by any theory or explanation, it is believed that the catalyst functions as a source of sulfur and enhances the quality

of the fine closed cells in the expanded product. The amount of curing agent typically corresponds to about 0 to about 5 wt.% of the composition prior to expansion.

The inventive composition can also comprise at least one supplemental  
5 polymers. An example of a suitable supplemental polymer comprises  
polybutadiene rubber, ethyl vinyl acetate, ethylene propylene diene monomer  
(EPDM), ethylene-acrylic acid polymer such as Primacor™ 5990 polymer supplied  
by The Dow Chemical Company, Midland, Michigan. The amount of optional  
supplemental polymer normally corresponds to about 5 to about 10 wt.% of the  
10 composition.

Further, the composition can also comprise at least one additive such as a  
colorant, tackifier, filler, plasticizer, processing oil, antimicrobial agents, UV  
curing agents, magnetic/magnetisable materials, among others. One suitable  
additive comprises EPDM. While any desirable colorant can be added to the  
15 composition, green or blue colorant supplied by Akron Chemical Company,  
Akron, Ohio as Akrochem 626 and 633 powder are effective. The total amount of  
additives, if present, corresponds to about 0 to about 5.0 wt. % of the composition  
before expansion. Virtually any additive can be added so long as the additive does  
not adversely impact the processability or expanded composition characteristics.  
20 In some cases for ease of handling, additives to the inventive composition (e.g.,  
colorant, tackifier, filler, plasticizer, processing oil, antimicrobial agents, among  
others), are blended into pellets and subsequently combined with the remaining  
components of the inventive composition.

While the presence of ionomeric compounds does not adversely impact the  
25 utility of the inventive composition, in one aspect of the invention the composition  
can be substantially free of ionomeric compounds. By "substantially free" it is  
meant that the composition has less than about 20 parts or 5.5 wt. % of ionomeric  
compounds, e.g., usually about 0 wt.% of ionomers. Examples of such ionomeric



compounds that may be obviated by the instant invention are disclosed in the aforementioned U.S. Patent No. 5,266,133. The ability to obviate ionomeric compounds reduces cost of the composition as well as enhances processability.

The inventive composition can be produced by mixing the components in any suitable apparatus, e.g., a dispersion mixer or twin screw, or continuous mixer. With the exception of the optional processing oil/plasticizers, the components of the inventive composition are solids under ambient conditions. Once mixed, the combination can be shaped by employing any expedient method such as blow molding, injection molding, compression molding, die cutting, extrusion, among other methods. Depending upon the configuration of the shaped inventive composition, normally injection molding or extrusion is preferred. For example, the inventive composition can be fabricated to possess the configuration of Figures 1A and 1B (described below in greater detail) by employing a single cavity injection mold, or a single cavity profile extruder. Injection molding can employ a Toyo Model TM200 molding machine with a water jacket around the barrel set at about 160F, a mold temperature set at about 70F, and a cycle time of approximately 30 seconds. Extrusion can employ conventional equipment and extrude a length of material having the same cross-section as an injection molded component. When extruding, the length of the material can be continuous and then cut at suitable increments, e.g., four (4) inch increments. An example of a conventional extruder comprises a 12/1 extruder with a standard flight screw, with a feed rate of about 150 lbs/hr, 160 F feed temperature, 200 F barrel temperature, and 200 F profile extrusion temperature. Normally, the extruded profile is immediately cooled by a chilled water bath to help maintain its shape. The extruded profile can possess any suitable configuration such as a circle, oval, square, pentagon, curvilinear shapes, among others.

The inventive composition can be shaped into a two or three dimensional configuration, or pumped to a location prior to expansion. For example, the composition can be injection molded into a hollow or solid cylindrical shape that is in turn located within an automotive cavity during assembly, e.g., formed

reinforcement tubes/channels, rocker panel or pillar cavities, among other areas/cavities. After being properly positioned (e.g., within an automotive cavity), the composition expands when exposed to the relatively high temperatures employed in subsequent processing, e.g., bake cycles, electrodeposition, painting,  
5 among other assembly procedures.

The inventive composition can be associated with or adhered to a virtually unlimited array of substrates such as electrocoated surfaces, e.g., panels including automotive components, cold rolled steel, galvanized surfaces, galvanel surfaces, galvalum, galfan, among others. The substrate or surface that contacts the  
10 inventive composition can also comprise a painted surface, ceramic, glass, thermoplastic, thermosets, among others.

In one aspect of the invention, the inventive composition is employed as a component of a composite structure. That is, the composition can be located or sandwiched between at least two metal layers thereby forming a so-called  
15 constraint layer damper. The composition may also be shaped into a thin-walled article having a continuous surface and at least one internal cavity. The composition can also be shaped to produce the articles disclosed in U.S. Patent No. 5,678,826.

In another aspect, the instant invention relates to an expandable material  
20 having a predetermined configuration or shape. In particular the expandable material can be configured into a shape that retains the expandable material at or within a defined location, e.g., an expandable material comprising an acoustical material located within an automotive cavity. The expandable material can be shaped so as to be self-retaining. By "self-retaining" it is meant that the  
25 expandable material after being placed in a defined location and position/orientation maintains the placement for a predetermined length of time (e.g., until being heated to expand) without utilizing separately applied fasteners. Self-retaining properties can be achieved by shaping the expandable material into a

clip, wedge, strap, bolt, among other shapes designed to mechanically maintain the expandable material at a predetermined placement. The self-retaining properties can also be achieved by compression fitting. While the self-retaining expandable material can be produced from any suitable composition, the composition

5 disclosed herein is particularly useful. For example, a self-retaining expandable can be formed from the inventive composition such that the expandable material has a unitary structure that includes a fastener. That is, the fastener would function to retain the expandable material in a predetermined location and expand (upon heating) to assist in sealing. The unity self-retaining structure can be tailored to

10 have a configuration including an integral fastener for a specific area, void or cavity to be sealed.

In a further aspect, the instant invention relates to an expandable material having a predetermined shape or configuration and having at least one fastener that retains the expandable material at a predetermined location. The fastener can

15 maintain the fastener at any suitable predetermined location such as an automotive front and/or rear "A"-pillar, "B"-pillars, "C"-pillar, among other locations where it is desirable to position an expandable material adjacent to a member to be sealed. By "adjacent" it is meant term "adjacent" as used in this specification and the claims, unless expressly stated otherwise, means two components that are in contact with each

20 other, are next to each other with a space separating them, or are next to each other with a third component in between. By "member to be sealed" it is meant that the material contacts the member either prior to, during or after completing expansion. The member to be sealed can be at least partially embedded or penetrated by the expanding material. The fastener can be attached to or incorporated within the

material prior to expansion. While any suitable fastener can be employed, examples of suitable fasteners comprise at least one member selected from the group of blades, pins, push-pins, clips, compression fit fasteners, among other fasteners that are capable for maintaining a shaped expandable composition in a  
5 predetermined location without adversely affecting the expansion or performance of the composition. Specific examples of suitable fasteners are described in aforementioned US Patent Nos. 5,040,803 and 5,678,826.

Certain aspects of the invention are better understood when referring to the Drawings. Referring now to the Drawings, Figure 1A illustrates an expandable  
10 material 10 of the instant invention. The expandable material possesses a circular gripping area 11. The portion 12 of material 10 that is adjacent to an opening in the circular gripping area 11 can function to improve the durability of the material 10 and/or provide increased material for subsequent expansion. The expandable material 10 is retained or clipped around a first automotive member (not shown)  
15 having a generally circular cross-section. The expandable material 10 generates a sufficient compressive strength to maintain the material at a predetermined location. The portion 13 of material 10 defines an opening 14. The width 15 of opening 14 is greater than or equal to the distance between a first automotive member within area 11 and a second automotive member (not shown) in contact  
20 with portion 12' and 12''. This distance permits the material to grip the first automotive member while also being compressed between the first and second automotive members. The length 16 of opening 14 causes or is sufficient to provide a volume of expandable material between the first automotive member and the second automotive member, and to add strength to the gripping action of area  
25 11. The length of 16 will increase or decrease as the diameter of 11 increases or decreases, respectively. The material can possess a wide range of dimensions;

however, normally, the wall thickness shown at portion 17 is about 2 to about 4 mm, dimension 14 about 2 to about 4 mm, the dimension 16 about 25 to about 35 mm and the overall length of 10 about 25 to about 45. When the expandable material is obtained by extrusion the length of 16 can be greater than 20mm.

5           When the material is exposed to sufficient heat (e.g., about 250 to about 375 F), the aforementioned expansion agent causes substantially all of the material to increase in volume and bond to adjoining surfaces, e.g, metal surfaces. While the material illustrated in Figure 1A is intended to contact an automotive door intrusion beam and the interior surface of the door, the composition can also be  
10   shaped for use as a sound damper/absorber in an "A" pillar, rear trunk sealant, among other areas in an automobile for use in controlling sound, water, wind and dust.

Referring now to Figure 1B, Figure 1B illustrates the expandable material illustrated in Figure 1B in cross-section format. While the composition shown in  
15   Figure 2 is intended to be affixed to a beam having a circular cross-section, the composition can be employed with beams or members having a virtually unlimited array of cross-sections. The composition also can be molded into a wide variety of shapes, e.g., strips, rods, curvilinear, among others, and sizes.

Referring now to Figure 2A, Figure 2A illustrates an expandable material  
20   having a similar configuration to that illustrated in Figures 1A and 1B except that the expandable material 20 has an enclosed gripping area 21. The expandable material illustrated in Figure 2A is configured such that the material can be inserted onto another member, e.g., a circular cross-section intrusion beam. Gripping area 21 includes protuberances 22 that are compressed when another  
25   member, e.g., a pipe, is inserted through material 20. By compressing protuberances 22, friction is created between the protuberances and the outer surface of the inserted member and thereby functioning to maintained material 20 at a fixed location upon the member.

Material 20 can define at least one slot or groove 23. These slots or grooves 23 provide locations where the material 20 can be compressed or bent. The ability to bend the material 20 permits locating the material at a given location without breaking or cracking the material.

5        Protuberances 22 can possess any suitable configuration. One such configuration is illustrated in Figure 2B. Referring now to Figure 2B, Figure 2B illustrates the expandable material illustrated in Figure 2A in cross-section format. The end of protuberance 22 has a radius 24 that terminates at each end of the opening or hole 25 defined within material 20. The terminating radius permits  
10        more expedient insertion of a member into or through material 20.

Referring now to Figures 3A-3C, Figures 3A-3C illustrate a further aspect of the invention wherein an automotive sealant comprises an integral fastener that is employed for maintaining the inventive expandable composition in a predetermined position, e.g., self-retaining. Expandable material 30 having a  
15        integral clip type fastener 31 (also comprising the inventive expandable material) that maintains material 30 adjacent to and within an automotive A-pillar (not shown). Fastener 31 also includes a leg or protuberance 32 that extends into the A-pillar. Material 30 defines openings 33 and 34. These openings can be employed for reducing mass (and material costs), enhancing flow of heat through  
20        the expandable material (thereby ensuring uniform expansion and lower activation temperature) and permitting fluids to flow through the material (e.g., automotive e-coat, metal treatments, among other fluids). Material 30 comprises extensions 35 and 36 that extend along an exterior surface of the A-pillar. The material 30 is attached to an A-pillar by inserting fastener 31/32 into the A-pillar such that  
25        extensions 35 and 36 contact the exterior surface of the A-pillar. The distance shown by 37 corresponds to the thickness of the A-pillar. When material 30 is exposed to an adequate amount of heat, all of material 30 (including fastener 31 and extensions 35/36) expands thereby sealing the A-pillar.

Referring now to Figures 4A-4C, Figures 4A-4C illustrate an expandable material having a similar configuration to that illustrated in Figures 3A-3C except that the expandable material 40 includes an expandable clip type fastener 41 that is oriented toward extension 42. Material 40 defines an opening 43 that functions in the manner described above in connection with openings 33/34. While material 40 can be employed for a wide range of end-uses, material 40 is particularly suited for sealing an automotive front B-pillar.

Referring now to Figures 5A-5C, Figures 5A-5C illustrate an expandable material having a similar configuration to that illustrated in Figures 3A-4C except that material 50 includes an expandable fastener 51, protuberance 52, opening 53 and extension 54. Material 50, similar to the materials illustrated in Figures 1-4 can be injection molded, can be fabricated into a wide range of configurations. The particular configuration illustrated in Figures 5A-5C is especially suited for sealing an automotive C-pillar.

Referring now to Figure 6, Figure 6 illustrates a self-retaining expandable material 60 that employs compression fitting. Material 60 comprises shank portion 61, compressible side portions 62 and 63 and end 64. Material 60 can be inserted into a desired location (e.g., within a cavity), by manually gripping shank portion 61 and inserting end 64 into the location until at least one of side portions 62 and 63 are compressed towards shank 64. Side portions 62 and/or 63 retain material 60 in a self-retained position. If desired, shank portion 61 can have embossed markings that can be used for gauging the depth that the material 60 has been inserted into a cavity.

If desired, the composition can incorporate a reinforcing member.

Examples of such reinforcing members comprise glass mesh, mats, plastic or nylon supports, among other materials capable of surviving the expansion temperature and enhancing the structural integrity of either the unexpanded or expanded composition.

In addition, at least a portion of the inventive composition can be laminated with a film, foil, web, sheet, among others. The laminate can be a temporary component of the composition such as a release film and/or permanently in contact with the composition. While any suitable laminate can be employed, examples of such laminates are disclosed in U.S. Patent Nos. 4,803,104 and 6,030,701; the disclosure of which are hereby incorporated by reference.

While the above Description emphasizes expandable compositions for use in automotive applications, the inventive composition can be employed in a virtually unlimited array of applications. Examples of such applications can include one or more of sealants for aircraft, golf cars, agricultural equipment, marine vessels, an insulating member, a residential or industrial sealant, among other applications. The inventive compositions can be extruded, pumped into a desired location, sprayed, preformed (e.g., injection molded), among other methods for using sealants.

The following Examples are provided to illustrate not limit the scope of the invention as defined by the appended claims. The percentages in these Examples are weight percent (%).

#### EXAMPLE 1

A composition was prepared by combining 100 parts per hundred resin (phr) of base polymer (Bynel™ 3860 supplied by the DuPont Company), 1.5 phr of hydrocarbon based process oil (Tufflo® 500 WsChem-Hall Inc.), 6.7 phr of Piccotac® hydrocarbon resin, 0.7 phr pounds TMTD™ supplied by AkroChem, and 10 phr of expansion agent (6.7 phr of Celogen OT and 3.3 phr of Celogen 765). 0-1 phr of peroxide supplied by Akrochem.

#### EXAMPLE 2



A composition was prepared by combining 100 phr of base polymer (Bynel™ 3860 supplied by the DuPont Company), 20 phr ethylene copolymer (Primacor 5990 supplied by Dow Chemical), 12 phr of expansion agent (8 phr of Celogen OT and 4 phr of Celogen 765), 8 phr of hydrocarbon resin and 0.8 phr  
5 TMTD™ (supplied by AkroChem), and .5 pounds BIK-OT (supplied by Uniroyal Chemical Company). 0-1 phr of peroxide supplied by Akrochem.

### EXAMPLE 3

A composition substantially the same as that disclosed by Example 2 was  
10 prepared with the exception that 0.04 phr of colorant (supplied by AkroChem) was added.

### EXAMPLE 4

The composition of Examples 1-3 were prepared by admixing the base  
15 polymer and, if present, 14% supplemental polymer (Primacor™ ethylene acrylic acid polymer) together in a Baker-Perkin dispersion mixer. About 3.5 pounds (0.97%) of the aforementioned light processing oil was added to the mixer and mixed for 5 to 10 minutes. The 0-2% curing agent (TMTD™ tetramethylthiuram disulfide) and expansion agent (Celogen™ 765) were added to the mixer, and the  
20 combination was mixed for 3 to 5 minutes. The remaining processing oil was added and mixing continued for 3-5 minutes. A blue colorant and additional expansion agent (Celogen™ OT) were added to the mixer and mixed for 3 to 10 minutes.

The aforementioned expansion agents had been pre-treated with 10-28%  
25 naphthenic binder supplied by Polychem or ElastoChem. The pre-treated expansion agents possessed at least about 90% of the activity of untreated expansion agents.

The mixed composition comprised pellets or particulate of base polymer substantially uniformly coated. The composition has no reportable dusting characteristics.

5

#### EXAMPLE 5

The compositions of Example 4 are dispensed into 5 gallon to 500 pound containers. The composition is then shaped by being injection molded in a Boy 30 Ton or Toyo Model No. TM200 injection molding apparatus to form an injection molded part. The injection molded or extruded article is baked at a temperature of  
10 about 300 to 400 F. The baking in turn causes the expansion agent within the article to become active thereby expanding the article's volume by at least 600%.

#### EXAMPLE 6

15 The compositions of Example 4 are dispensed into an extruder. The composition is extruded to form a sheet structure. The composition is extruded by a 12/1 extruder that has been modified to include a compression flight screw. The following outlines the extrusion parameters: 180 lbs/hr feed rate, 160 F feed temperature, 200 F compression section temperature; and 220 F head/die  
20 temperature. The extruded article is expanded by being heated.

#### EXAMPLE 7

Example 2 was repeated with the exception that ethylene copolymer was replaced  
25 with 8 – 20 phr of polybutadiene polymer. The polybutadiene was supplied by JSR Corp.

EXAMPLE 8

This Example describes making an injection molded composition that was employed as a stiffener on an intrusion beam within an automotive passenger door. The components of the composition are listed in the following Table.

5

TABLE

<u>Supplier</u>	<u>Material</u>	<u>Phr</u>
Ameripol-Synpol	SBR rubber	100
Petrolite	Process Aid	87.5
Exxon	Hydrocarbon resin	6.3
DuPont	EVA resin	300
Polychem	Blowing agent	21.8
Atochem	Peroxide	6.3
Akrochem	TMTD	6.3
Cabot	Carbon Black	1.9
Mozel	Filler	100

The heat expandable composition was mixed in a lab BakerPerkins dispersion blade. The mixed composition was injection molded into a single  
10 cavity mold having the shape substantially as illustrated in Figures 1A and 1B.

The injection molded article was located or clipped about an intrusion beam. The beam was introduced into a forced air oven chamber and exposed to a temperature of about 325F for a period of twenty minutes. The composition expanded between the beam and an adjacent steel member (that represented the  
15 interior portion of an automotive door skin). The composition adhered to the interior portion of the door skin as well as the intrusion beam thereby reducing panel mobility. By reducing panel mobility the inventive composition reduces

noise caused by rattles, improves strength of the door, among other desirable properties.

Examples 9-11 demonstrate injection moldable compositions that were  
5 fabricated in accordance with the method of Example 8.

## EXAMPLE 9

TRADE NAME	COMPONENT	AMOUNT
Bynel 3860	Maleic anhydride modified copolymer of ethylene and vinyl acetate	100 phr
Picotac B	Hydrocarbon resin	6.7 phr
Tufflo 500	Hydrocarbon process oil	1.5 phr
TMTD	Tetramethylthiuram disulfide	0.7 phr
Celogen OT	Hydrazide expansion agent	6.7 phr
Celogen 765	Expansion agent	3.3 phr

## EXAMPLE 10

TRADE NAME	COMPONENT	AMOUNT
Bynel 3860	Maleic anhydride modified Copolymer of ethylene and vinyl acetate	100 phr
Primacore 5990	Acid mod. Ethylene copolymer	100 phr
Picotac B	Hydrocarbon resin	0-20 phr
Tufflo 500	Hydrocarbon process oil	6-8 phr
TMTD	Tetramethylthiuram	0-1.8 phr
Peroxide	Commodity	0-1 phr
Celogen OT	Expansion agent	0-1 phr
Celogen 765	Expansion agent	6-8 phr
Bik-OT	Expansion agent	0-4 phr

## EXAMPLE 11

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TRADE NAME	COMPONENT	AMOUNT
SBR 1009	Styrene Butadiene	46.2 phr
Primacor 5990	Acid mod. Ethylene copolymer	30.1 phr

SBR 1205	Styrene Butadiene	23.1 phr
Elvax 260	Ethylene Vinyl Acetate	100 phr
RB 8101,2	Polybutadiene	76.9 phr
195 wax	Clay treated wax	33.8 phr
Resin 7312	Hydrocarbon resin	3.8 phr
QW200	Calcium Carbonate	61.5 phr
Carbon black	Organic Peroxide	3.8 phr
TMTDT	Tetramethylthiuram disulfide	5.4 phr
Celogen OT	Hyrazide	15.4 phr

Example 12 illustrates a moldable composition that was fabricated to possess the configuration illustrated in Figure 6.

5

## EXAMPLE 12

Material Name	Supplier	Quantity	Wt %	Material type	
SBR 1009	Ameripol-Synpol	165	30.05	styrene butadiene rubber	
Nordel IP 4725	Dupont-Dow	150	27.32	ethylene propylene rubber	
RT2730 (APAO)	Huntsman	100	18.21	Poly alpha olefin	
MV2514	Exxon	50	9.11	Ethylene vinyl acetate	
Gilsonite Multi-grade	Lexco	15	2.73	Hydrocarbon resin	
Carbon Black Regal 300	Cabot	2	0.36	carbon black	
Celogen AZ180	Uniroyal	50	9.11	Azodicarbonamide	
Superfine Sulfur	Akrochem	5	0.91	sulfur	
Zinc Oxide	Morton-Myers	10	1.82	zinc oxide	
Industrene R	Barton Solvents	2	0.36	stearic acid	
		549			

The heat expandable composition of Example 12 was mixed in a lab BakerPerkins mixer with dispersion blade. The following mix procedure was utilized.

- 10           SBR rubber, EPDM rubber, Eva resin, and approximately 1/3 of the APAO were blended. Blend was allowed to reach a temperature of 140°F, and mix until homogeneous. The mixer was stopped, and the Gilsonite, zinc oxide, stearic acid, blowing agent, sulfur, carbon black and the remainder of the APAO were added

The composition was mixed until homogeneous, and attained a mix temperature of approximately 155°F. The mixed composition was extruded and die cut into the configuration shape illustrated in Figure 6.

- The shaped article was located in opening of a steel 1x2 tubular frame rail.
- 5 The frame rail was introduced into a forced air oven chamber and exposed to a temperature of about 385F for a period of twenty minutes. The composition expanded and filled the interior of the frame rail. The composition adhered to the interior portion of the rails.

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THE FOLLOWING IS CLAIMED:

1. An unexpanded composition comprising a combination comprising a modified ethylene copolymer base polymer, at least one hydrazide expansion agent, at least one hydrocarbon resin and at least one sulfur containing curing agent.
2. An injection molded composition comprising a combination comprising at least one copolymer base polymer, at least one expansion agent, at least one hydrocarbon resin and at least one curing agent wherein said composition is substantially free of ionomeric compounds.
3. The composition of Claim 1 or 2 wherein the base polymer comprises a modified ethylene copolymer and corresponds to about 50 to about 90 wt.% of the composition.
4. The composition of Claim 1 or 2 wherein expansion agent comprises at least one member selected from the group consisting of azodicarbonamides, p,p'-oxybis(benzene-sulfonyl hydrazide) and diphenylozide-4,4'-disulphohydrazides.
5. The composition of Claim 1 or 2 further comprising at least one processing oil.
6. The composition of Claim 1 or 2 wherein the hydrocarbon resin comprises an aliphatic hydrocarbon resin.

7. The composition of Claim 1 or 2 wherein the curing agent comprises tetramethylthiuram disulfide.

8. The composition of Claim 1 or 2 wherein the composition further  
5 comprises an ethylene acrylic acid copolymer.

9. The composition of Claim 1 or 2 wherein the composition expands at least 500% when exposed to a temperature of at least about 300 F.

10. The composition of Claim 1 or 2 wherein composition further  
10 comprises at least one additive selected from the group consisting of colorants, tackifiers, fillers, UV curing agents and plasticizers.

11. An expandable composition substantially having the  
15 configuration illustrated in any one of Figures 1 through 6.

12. A self-retaining expandable composition comprising a combination comprising at least one base polymer, at least one supplemental polymer, at least one expansion agent and at least one filler.

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13. The expandable composition of Claim 1 further comprising at least one fastener and defining at least one opening.

14. Use of the composition of Claim 1 as an automotive sealant.

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1/3

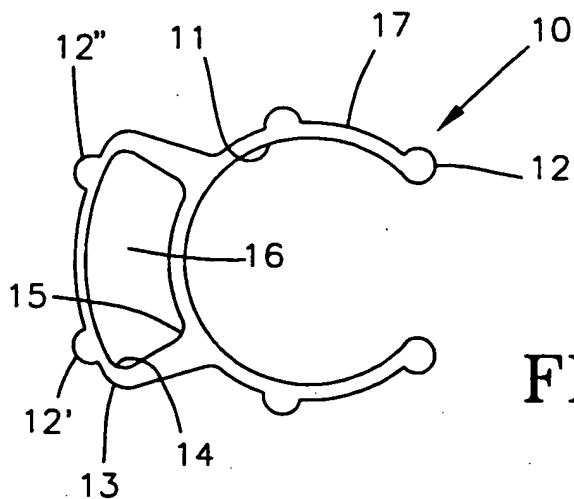


FIG. 1a

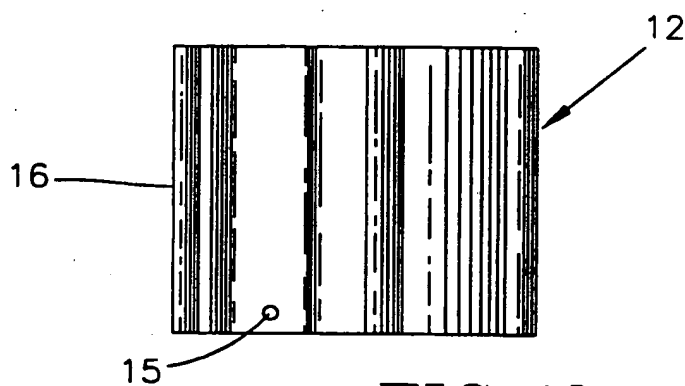


FIG. 1b

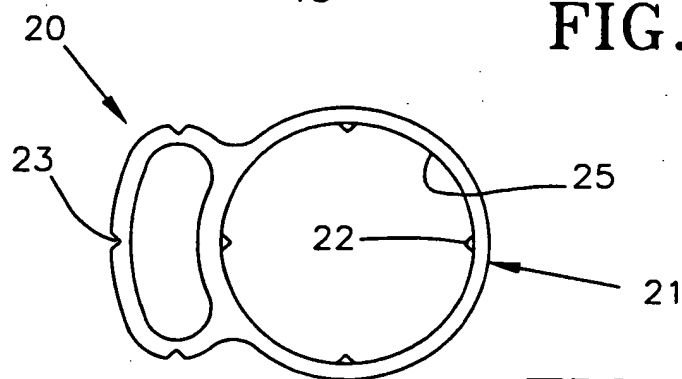


FIG. 2a

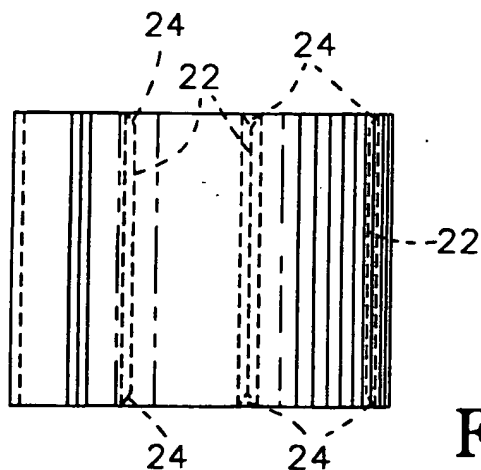


FIG. 2b

SUBSTITUTE SHEET (RULE 26)

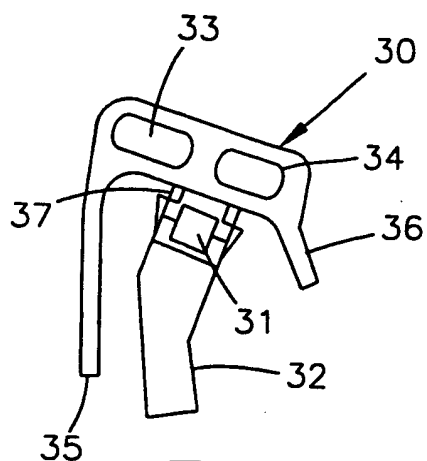


FIG. 3a

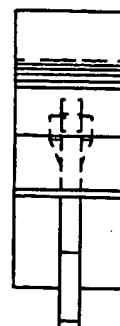


FIG. 3b

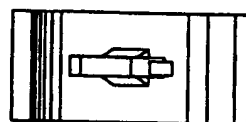


FIG. 3c

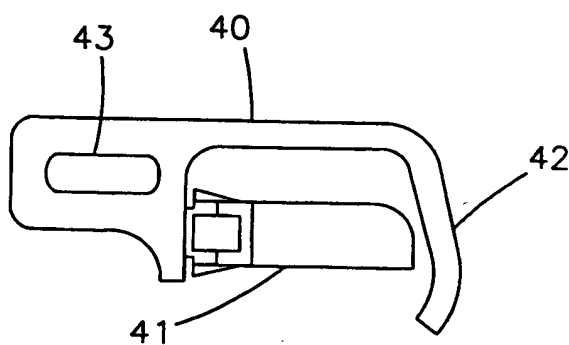


FIG. 4a

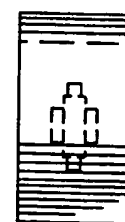


FIG. 4b

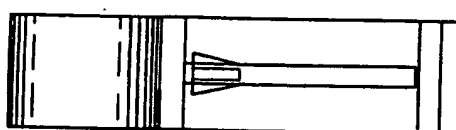


FIG. 4c

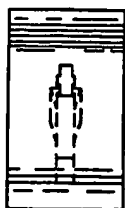


FIG. 5b

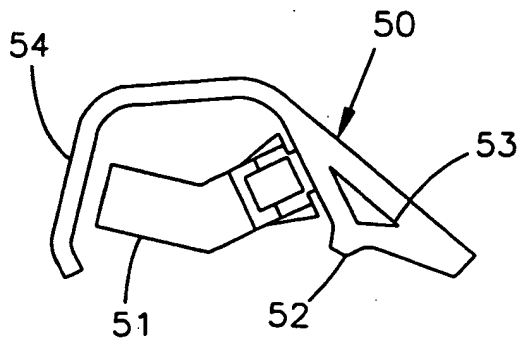


FIG. 5a

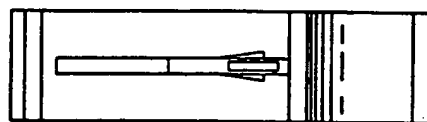


FIG. 5c

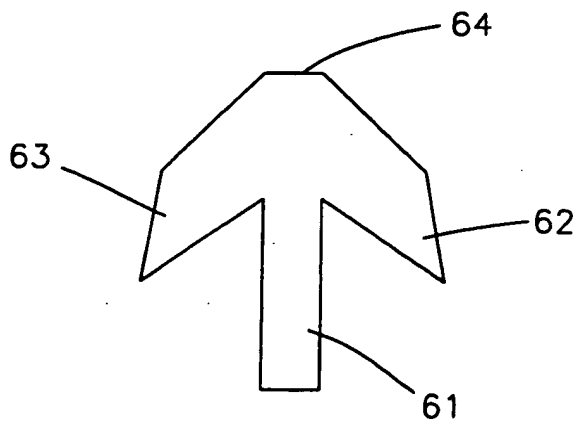


FIG. 6

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/29615

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08L23/08 C09K3/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08L C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 266 133 A (BOOS ROMAN C ET AL) 30 November 1993 (1993-11-30) cited in the application	1-4, 6, 10, 14
X	the whole document	12
A	US 5 373 027 A (BOOS ROMAN C ET AL) 13 December 1994 (1994-12-13) cited in the application	1-4, 6, 10, 14
X	the whole document	12
X	US 5 118 531 A (PETERSEN HENNO A ET AL) 2 June 1992 (1992-06-02) the whole document	12
X	US 4 680 316 A (DOUGLAS WILLIAM A) 14 July 1987 (1987-07-14) the whole document	2, 6, 10

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

13 February 2001

Date of mailing of the international search report

20/02/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Puetz, C

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 00/29615

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
E	US 6 150 428 A (BLANK NORMAN E ET AL) 21 November 2000 (2000-11-21) the whole document	2-4,6, 10,12

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Information on patent family members

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